Some Dyes as Corrosion Inhibitors for Aluminium-Copper Alloy in Sodium hydroxide

J.D.Talati and B.S.Patel

Shri U.P.Arts, Smt. .M.G.Panchal Science & Shri V.L.Shah Commerce College, PILVAI-382 850 (India).

Study of some dyes like phenolphthalein, eosin, flourescein-Na, methyl red, congo red, methylene blue and safranine-T as inhibitors of corrosion of B26S aluminium (Al-4% Cu) in sodium hydroxide solutions shows that inhibition effciency increases with inhibitor concentration but decreases with increase in alkali concentration or with a rise in temperature. The efficiency of phenolphthalein, eosin and flourescein-Na decreases while that of methylene blue and safranine-T increases with the period of immersion.

A specimen of B26S aluminium in 0.1 M NaOH shows a steady state potential of -1400 mV *vs* S.C.E. This increases slightly in presence of safranine-T, cosin, methyl red and flourescein-Na. Phenolphthalein, methylene blue and congo red do not appear to have any effect. Under galvanostatic polarisation conditions, the anode appears to be polarised to a slightly greater extent than the cathode. The linearity of the plots of log inhibitor concentration *vs* log inhibitor efficiency shows that the inhibitors function through adsorption following Freundlich isotherm.

Thermodynamically aluminium is a highly reactive metal. E°_{red} = -1.67 V; $\Delta G^{\circ}_{Alumina}$ = -1582.4 kJ.mol^{-1} [1]. Hence aluminium surfaces are usually covered with an extremely thin but remarkably tight, adherent and protective oxide film. The film is generally stable in solutions of pH 4.5 - 8.5, but due to its amphoteric nature, it fails to protect aluminium in strongly acid or strongly alkaline media [2]. Compared to pure aluminium, Al-Cu alloys possess high strength to weight ratio but lower corrosion resistance.

Prior to anodising or decorative finishing treatment of aluminium, pickling in caustic alkali for degreasing is a common practice [3]. As the dissolution rate of aluminium and its alloys is very high in strong alkalies, it is desirable to inhibit the solution used for pickling.

The corrosion of aluminium in sodium hydroxide solutions has been studied extensively. A vast spectrum of inhibitors has also been investigated in this context [4]. It has been reported that the inhibitors for aluminium work less efficiently in alkaline solutions than in acidic ones. Our earlier communications report on the inhibition of corrosion of 2S, M57S, B26S

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aluminium in NaOH solutions using various protective colloids [5,6a], of B26S alloy with dihydroxy-benezenes [6b] & various phenols [6c-f] and 3S alloy in KOH solutions by aldehydes & dyes [7a,b]. Joshi and Talati have also studied dyes as inhibitors in solutions of aliphatic amines [7c].

In the present work the inhibition of corrosion of B26S aluminium in sodium hydroxide solutions containing some dyes has been reported.

EXPERIMENTAL TECHNIQUE

The chemical composition of B26S aluminium alloy (supplied by Indian Aluminium Co. Ltd., Bombay) was determined by standard methods and found to be: Cu-3.88; Mn-0.87; Fe-0.71; Si-0.59; Mg 0.32%; Al-remainder.

Weight loss Studies

Rectangular specimens of size 5 cm x 4 cm, with a small hole of about 2 mm diameter near the upper edge of the specimen, were used for determining the corrosion rate. These specimens were polished as described earlier [9] using tripoli composition followed by jeweller's rouge (Canning Mitra Phoenix Ltd., Mumbai). The test specimens were suspended by glass hook and dipped in corroding caustic soda solutions (concentration range 0.01 - 1.0 M) containing controlled additions of various dyes. Temperature was adjusted at 30±0.5°C (unless otherwise specified). Only one specimen was suspended in each beaker containing 230 ml of test solution and left exposed to the air. At the end of the test period, the specimens were cleaned in a dichromate-phosphoric acid mixture [10]. Duplicate experiments were performed in each case and the mean value of the weight loss has been recorded.

Potential Measurements

Circular metal coupons of 2.88 cm diameter and a handle of 3.22 cm long and 0.48 cm wide were used. The weight of the coupon was approximately 1.64 g. The handle and the back of the coupon were coated with a mixture of perspex and wax from chloroform solution, leaving only a circular portion of apparent surface area 6.54 sq.cm. This was exposed to the corrosive medium in beaker-type cell with Luggin's capillary as near to the electrode surface as possible. The change in potential (to ±5 mV) was measured using a D.C.microvoltmeter (Philips India Ltd.) and a saturated calomel electrode.

RESULTS AND DISCUSSION

Inhibitor efficiency I, is defined as:

$$I = \frac{W_u - W_i}{W_u} \times 100\%$$

where W_i and W_u are weight losses of metal in inhibited and uninhibited

solutions respectively.

Corrosion in Sodium hydroxide

Specimens immersed in dilute NaOH solutions (<0.1 M) developed a film of grey to blakish-grey loose corrosion product which could easily be removed with a jet of water or by rubbing it with a rubber bung. On cleaning, the specimens revealed a bright, matt surface, indicating general etching of the metal. The greyish film was thicker at higher concentrations of NaOH and on cleaning the specimens, some pits were found on the metal surface. In all solutions, the attack appeared to be more severe at the edges.

At low concentrations of NaOH, the corrosion rate (mg/dm²/h) decreases with time; at higher concentrations, it increases; at intermediate concentration, it is almost constant with time (Fig 1A)

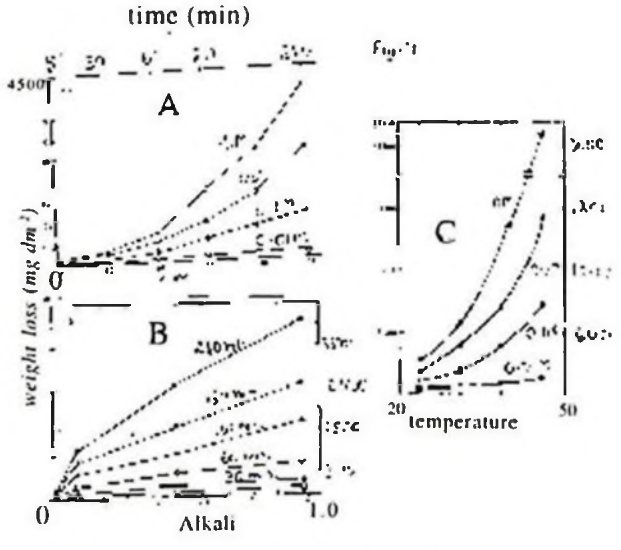


Fig.1 Weight loss of B26S Al in Alkali under Different Conditions

A Weight loss vs Time (Min) at different concentrations of alkali

B Weight loss vs Alkali concentration at different times

C Weight loss vs temperature at different alkali concentrations

all for periods up to 4 h immersion. The decrease in rate at lower concentration may be traced to the depletion of alkali in the solution by the corrosion process or by absorption of CO_2 from the air, the most dilute solutions being the most affected.

The corrosion rate is seen to increase with alkali concentration (Fig 1B). This may be due to the formation of the complex aluminate ion in concentrated alkali. Aluminate complex keeps the concentration of the Al^{3+} ion in solution very low. Copper from the alloy entering the solution as a result of the corrosion process could also enhance corrosion.

As the temperature of the NaOH is increased, the rate of corrosion also increases; it is almost doubled for every 10° rise in temperature (Fig.1C)

The energy of activation (E) is calculated using the equation:

$$\log \frac{\rho_2}{\rho_1} = \frac{E}{2.303\ R} \left\{ \frac{1}{T_1} - \frac{1}{T_2} \right\}$$

where ρ_1 and ρ_2 are the corrosion rates (mg/dm²/h) at the temperatures T_1 and T_2 (°K) respectively. The E values calculated at different concentrations are presented in Table 1.

The E values at low concentration are very low and anomalous. This could be attributed to the depletion of OH^- near the specimen. From the values at other concentrations, average E is calculated

Table 1

Energy of Activation (E) for Corrosion of Al-4%Cu Alloy in NaOH of Different Concentration

[NaOH] M	E,kJ/mol for Temperature Range 20-30°C	30-40°C	40-50°C
0.01	(31.3)	(21.4)	(32.8)
0.1	53.3	55.8	51.4
0.5	58.8	44.4	56.6
1.0	55.6	57.6	72.9

Mean value of E = 56.2 kJ/mol

and included in the Table. The E values were also determined from slopes of plots of log ϱ *vs* 1/T. The values were found to be almost in agreement with those obtained from the analytical equation.

Dyes as Corrosion Inhibitors

According the Evans [11] the inhibition of corrosion of aluminium in alkaline solutions is a difficult problem, probably because of the specific adsorption of OH^- on the metal surface. Antropov [12] also states that for a corrosion process occuring at a negative potential (such as the dissolution of aluminium or zinc in alkaline media), all organic compounds are repelled from the electrical double layer and effective inhibition is difficult. It is thus understandable that complete inhibition of aluminium or zinc in caustic alkali has not been reported so far. However, various azo dyes (like congo red & methyl red), xanthene dyes (like phenolphthalein, flourescein & eosin) and heterocyclic dyes (like sufranine-T and methylene blue) were examined in concentrations ranging from 0.01-1% in sodium hydroxide solutions of different molarities. The pH values of 1% aqueous solutions of inhibitors lie in the range 5.6 (methylene blue) to 8.3 (congo red) and these aqueous solutions do not corrode aluminium. The pH of 0.1 M NaOH was found to be 12.7 while the values for inhibited alkali (0.1 M NaOH + 1% inhibitor) were observed to lie in the range of 12.0 (methylene blue) to 12.5 (eosin), i.e., the dyes do not have much effect on the pH of the NaOH solution.

The specimens exposed to corroding solutions containing the dyes became covered with a film of the same color as that of the solution and the film could be removed easily with the cleaning solution.

Average Weight loss in 0.1 M NaOH (Statistical Considerations)

Many of the results on inhibitor efficiency mentioned in the present work

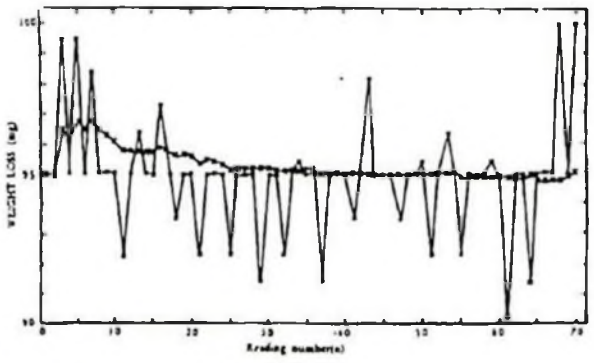


Fig.2 Variation of weight loss (mg) data; Replicate Values

Table 2

Statistical Analysis of Results from Fig 2

	Parameter	Definition	Value
01	No. of Readings	N	70
02	Range	Largest - Smallest	9.8 mg
03	Degrees of freedom	N - 1	69
04	Sum of Readings	Σx	6650.8 mg
05	Arithmetic mean (m)	$\Sigma x/N$	95.0 mg
06	Mean Deviation	$1/N\ \Sigma(X_i - m)$	0.89 mg
07	St.Deviation (s)	$\left\{\frac{\Sigma(X_i - m)^2}{N - 1}\right\}^{1/2}$	1.80
08	Variance	σ^2	3.24
09	Coeff. of Variation	σ/m	0.0189
10	Accuracy of Estimate for 95% probability	$m\pm\left\{\frac{2.06\ \sigma}{N^{1/2}}\right\}$	$m\pm0.4432$

were obtained by experiments in 0.1 M NaOH; so it was considered necessary to find a reliable value of the mean weight loss in 0.1 M NaOH. For this purpose a large number of replicate measurements were made (Fig 2) and the average value of the weight loss was evaluated from statistical considerations. Results of this analysis is given in Table 2.

Percentage Inhibition

Effect of Inhibitor Concentration

The numerical value of inhibitor efficiency depends on the particular inhibitor; however, in case of all the seven dyes in 0.1 M NaOH, the efficiency increases with inhibitor concentration but the inhibitor works relatively more effectively at lower concentration. Efficiency increases initially with inhibitor concentration but later, it tapers off (Fig 3A). The plots resemble adsorption isotherms. This confirms that adsorption phenomenon is occuring on the metal surface in case of all the seven inhibitors.

At 0.1%, the order of efficiency of different inhibitors is: flourescein - Na (60%) > safranine-T (59%) > phenolphthalein (44.4%) > methyl red > eosin > methylene blue > congo red (11.3%). With 1% inhibitor, the order is: flourescein - Na (70.5%) > phenolphthalein > eosin > methyl red > methylene blue (40.9%). The maximum

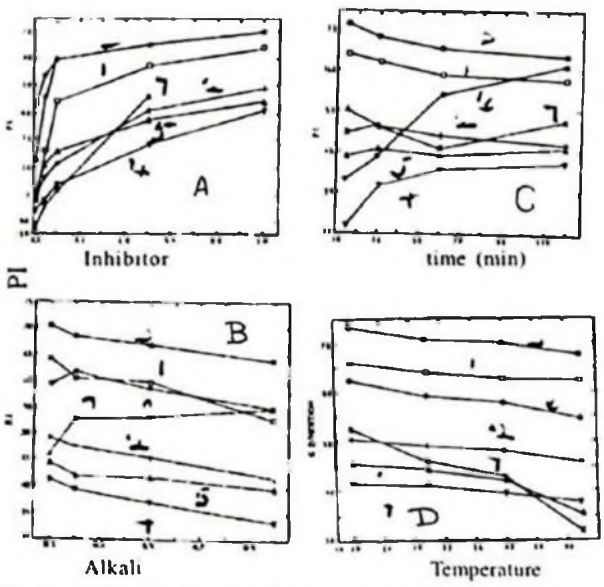


Fig.3 Percentage Inhibition (PI) under differnet conditions

A PI *vs* Inhibitor Conconcentration
B PI *vs* Alkali Concentration
C PI *vs* Time (min)
D PI *vs* Temperature

1. Phenolphthalein 2. Eosin 3. Fluorescein-Na
4. Methylene blue 5. Methyl red
5. Safranine-T 7. Congo red

concentration for methylene blue and safranine-T was only 0.5% and 0.1% respectively as the inhibitors were not soluble further.

Effect of Alkali Concentration

The effect of alkali concentration on the inhibitive efficiency of the dyes at a concentration of 1.0% is given in Fig.3B. It has been found that the efficiency of phenolphthalein, eosin, flourescein-Na, methyl red and methylene blue decreases whereas that of congo red increases slightly with increase in alkali concentration. In the case of safranine-T, the efficiency was found to be almost constant (58±3%) in the concentration range studied. Both safranine-T (0.1%) and congo red (0.5%) show an efficiency of about 55% in 1M alkali. At 1% concentration, the general order of efficiency of the inhibitors is found to be: flourescein-Na > phenolphthalein > eosin > methyl red > methylene blue.

Effect of Duration of Immersion

The effect of exposure period on inhibitor efficiency of different dyes at 1% concentration (0.5% for congo red and 0.1% in the case of sufranine-T) in 0.1 M NaOH is shown in Fig.3C. The results show that the efficiency of phenolphthalein, eosin, and fluorescein-Na decreases with the period of exposure, that of methyl red and congo red remains almost constant, while the efficiency of methylene blue and safranine-T increases with time. For a constant period, the efficiency is found to increase in the order: methylene blue < safranine-T < methyl red < congo red < eosin < phenolphthalein < fluorescein-Na (for 15 min) and in the order: methylene blue < methyl red < eosin < congo red < phenolphthalein < safranine-T < fluorescein-Na (for the 2 hr immersion period). During the test, fluorescein-Na gives maximum (69-77%) and methylene blue the minimum (27-42%) inhibition.

Effect of Temperature

In practice, the pickling of aluminium is carried out in alkali solutions at temperature ranging from 30°C to 80°C.

Table 3

Percent Inhibition (PI) and Energy of Activation E of B265 (Al-4%Cu) Aluminium in NaOH in Presence of Some Dyes

Specimen size 5cm x 4 cm; Immersion Period 1 hr; Alkali 0.1 M; Inhibitor Conc: 0.5% for congo red: 0.1% for safranin-T; All other cases 1.0 %

Inhibitor &Formula	M.W	P I at Dif Temp.				E kJ/mol in temp			Mean
		20	30	40	50	20-30	30-40	40-50	E
Nil - -	-	-	-	-	53.3	55.8	51.4	53.5	
Phenolphthalein $C_{20}H_{14}O_4$	318.3	66.0	64.1	62.7	62.4	57.5	59.2	51.8	56.2
Eosin $C_{20}H_6Br_4Na_2O_5$	691.9	50.4	49.1	48.0	45.4	54.4	57.5	54.8	55.6
Fluorescein-Na $C_{20}H_{10}Na_2O_5$	376.3	73.2	70.5	69.8	67.4	60.5	57.7	57.7	58.6
Methyl red $C_{15}H_{15}N_3O_2$	269.3	45.4	44.3	41.8	35.2	55.0	59.4	60.3	58.2
Congo red $C_{32}H_{22}N_6Na_2O_6H_2$	696.7	52.6	46.0	42.4	31.8	63.2	60.9	65.5	63.2
Methylene Blue $C_{16}H_{15}ClN_3S.3H_2O$	373.9	41.3	40.9	39.1	37.6	54.0	58.3	53.1	55.1
Safranine-T $C_{20}H_{19}ClN_4$	350.9	62.4	59.1	58.2	54.9	57.9	57.5	57.5	58.2

Fig.3D shows the effect of temperature on weight loss of B26S alumnium in 0.1 M NaOH containing different dyes. The rate of corrosion is found to increase (the efficiency decreases) with temperature of the sodium hydroxide solution (Table 3). The decrease in efficiency is 4% in the case of phenolphthalein and methylene blue and 21% in the case of congo red. The general order of efficiency of different inhibitors at 1% concentration in 0.1 M NaOH is found to be: fluorescein-Na > phenolphthalein > eosin > methyl red > methylene blue.

The values of energy of activation as calculated from the integrated form of the Arrhenius equation are given in Table 3. The E values in the inhibited alkali range from 55.1 to 63.2 kJ/mole, the values being slightly higher in inhibited than in uninhibited solutions.

Corrosion Potential and Polarisation Behaviour

Anodic and cathodic galvanostatic polarisation curves for B26S aluminium in 0.1 M NaOH alone and containing 1.0% concentration of the various inhibitors are shown in Fig.4.

A specimen of B26S aluminium, when immersed in 0.1 M NaOH developed a steady state potential of -1400 mV *vs* SCE. The corrosion potential was found to increase (become less negative) in presence of inhibitor (Table 4). Increase was maximum in the case of methyl red and minimum with 0.1% safranine-T.

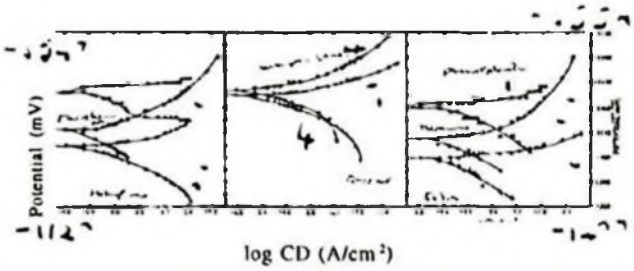


Fig.4 Effect of Current Density on Cathode and Anode Potentials of B26S aluminium (Al-4% Cu alloy) in 0.1 M NaOH
Inhibitor present: 0.5% congo red or 0.1% for safranine-T or 1.0% others.
1. Phenolphthalein 2. Eosin 3. Fluorescein-Na
4. Methylene blue 5. Methyl red
5. Safranine-T 7. Congo red

Phenolphthalein (1%), methylene blue (1%) and congo red (0.5%) did not appear to have any effect on the corrosion potential (or they polarise the anode and cathode to the same extent). Under galvnostatic polarisation conditions the anode appeared to be polarised to a slightly greater extent.

The Tafel parameters (anodic and cathodic Tafel slopes and also i_{corr} obtained by extrapolating Tafel lines) calculated from the polarisation data are given in Table 4. The inhibition efficiencies (calculated by extrapolation of cathodic Tafel lines to the open circuit potential) almost agree with those calculated from weight loss data.

Mechanism of Inhibition

Various theories have been put forward to explain the mechanism of corrosion by different types of inhibitors. Inhibitors of colloid type are said to be adsorbed uniformly over the entire metal surface [13]. Organic substances capable of forming onium ions give cations in acid solutions which would be adsorbed on the cathodic part of the metal surface [14]. This could act as a mechanical barrier for H^+ ions to reach the metal surface. If the inhibitor molecule is in an ionic form (eg. phenol), it may also get attached to the metal surface by electrostatic

Table 4

Tafel Parameters and Inhibitor Efficiencies of Some Dyes
speciman B26S Aluminium : medium 0.1 M NaOH
Surface area of the specimen = 6.15 cm^2; Temp = 30±0.5°C;
E= Energy transfer co-efficient : i_{corr} obtained by extrapolating Tafel slope

Inhibitor	OCP mV vs SCE	Tafel Slope Anodic	Tafel Slope Catho.	E Catho.	i_{Corr} A/cm² Catho. x 10^4	i_{Corr} A/cm² Anodic x 10^5	Inhibitor Efficiency from Catho.	Anod.	wt.loss
Nil	-1400	0.095	0.034	1.76	2.818	6.310	-	-	-
Phenolphthalein	-1400	0.040	0.033	1.82	9.505	3.162	66.3	49.9	64.1
Eosin	-1300	0.050	0.021	3.0	1.479	3.236	47.5	48.7	49.1
Fluoresein-Na	-1310	0.088	0.066	0.91	8.913	2.512	68.4	60.2	70.8
Methyl red	-1270	0.055	0.052	1.16	1.660	3.631	41.1	42.5	44.3
Congo red	-1390	0.051	0.041	1.47	1.738	3.467	38.3	45.1	46.0
Methylene Blue	-1400	0.051	0.125	0.48	1.738	3.715	38.3	41.1	40.9
Safranine-T	-1340	0.043	0.067	0.90	1.778	2.512	36.9	60.2	59.1

attraction to the anodic or cathodic sites, depending upon the charge on inhibitor molecule.

Most organic inhibitors are compounds with at least one polar functional group, having hetero atoms like nitrogen, sulphur, oxygen or in some cases, selenium and phosphorous. The polar unit is usually regarded as the reaction centre for the chemisorption process. In such cases, the adsorption bond strength is determined by the electron density on the functional atom and by the polarisability of the unit. According to Heckerman [15] amine type inhibitors have electron - donating ability and their action is attributed to the adsorption of the molecule on the metal surface through an unshared pair belonging to the nitrogen atom. The same is applicable for the atom of sulphur also. According to Hayakawa [16] *et. al.*, the choice between physical and chemical adsorption depends on the strength of the bond between the metal and inhibitor; chelation, for example, may result in chemisorption.

In the present case, the linearity of the plot of log (% inhibition) *vs* log (inhibitor concentration) (plot not shown) suggests that the inhibitor is adsorbed according to the Freundlich adsorption isotherm, (which is obeyed in the concentration range 0.01 - 1.0% for eosin, fluorescein and safranine-T and phenolphthalein). The adsorption can take place *via* the functional oxygen atom of the inhibitor molecule or it may be through the delocalised π - electrons in the case of the compounds containing an aromatic ring or a double bond.

The constancy of inhibitive efficiency of safranine-T with increase in alkali concentration or a slight increase in the case of congo red suggests that the interaction between the metal and the inhibitor is chemical: the adsorption bonds are stronger. This also shows that the adsorptivity of such inhibitors on aluminium is greater than that of OH^- ion [17]. The almost constant values of energy of activation in inhibited alkali suggest that the mechanism of action is almost similar in the case of all inhibitors. Further, almost similar values of E in inhibited as well as uninhibited alkali indicate that the behaviour of the inhibitor resembles that of stable poisons in heterogeneous catalysis, which as Taylor [17] has shown, do not affect the temperature coefficient of the reaction.

If the inhibitive power of the three classes of compounds are compared, it is observed that xanthene dyes (flourescein-Na, phenolphthalein and eosin and safranine-T) show better efficiency than the other three. The comparatively better efficiency of safranine-T as compared to eosin may be traced to the presence of four nitrogen atoms in the inhibitor molecule. The higher values of anodic slopes suggest that the inhibitors function through adsorption on the anodic portion of the corroding metal. Thus the higher efficiency of fluorescein-Na and

phenolpthalein may be traced to the fact that both exist in anionic form in solution and therefore, function through adsorption on the anodic region of the metal surface. The lower value of methylene blue may be due to the positive charge on the inhibitor molecule. In the case of other inhibitors steric hindrance may also be playing a part to reduce their efficiencies.

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